



Thermodynamics of hydrogen bonding of weak bases in alcohol solutions: Calorimetry of solution, IR-spectroscopy and vapor pressure analysis

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ABSTRACT

The properties of solutes and their reactivity in aliphatic alcohols significantly depend on the formation of hydrogen bonds. In this work, calorimetric, FTIR-spectroscopic and gas chromatographic vapor pressure studies of hydrogen bonds of weak bases in solution of aliphatic alcohols were carried out. Enthalpies of solutions at infinite dilution of ketones, nitriles and acetates in methanol and octan-1-ol were measured. Obtained from the calorimetric data, the enthalpies of specific interaction of weak bases in aliphatic alcohols unexpectedly found to be positive. IR spectra of solutions of ketones in aliphatic alcohols at infinite dilution were measured at different temperatures. Enthalpies of specific interaction in studied systems obtained from the spectroscopic data confirmed the endothermic process and are in good agreement with calorimetric results. Gibbs energies and entropies of specific interaction of weak bases in aliphatic alcohols were determined.

Obtained results show, that the hydrogen bonding process of weak bases in aliphatic alcohols differs substantially from the formation of complexes $1:1 \text{ ROH} \cdots \text{B}$ (B – weak proton acceptor) in aprotic media. The complicated process of hydrogen bonding of weak bases in aliphatic alcohols apparently is controlled by the entropy factor, because these values are above zero.

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1. Introduction

Aliphatic alcohols present an example of self-associated liquids, which physical and chemical properties are greatly affected by forming of hydrogen bonded complexes [1]. Hydrogen bonded clusters in alcohol medium can be varied by structure (linear, branched, cyclic) and composition (monomer, dimer, tetramer, etc.), and are in equilibrium with each other [1]. Various processes, realized in aliphatic alcohols, as well as the reactivity of the solute molecules in their medium, greatly depend on the hydrogen bonding with the solvent. Since aliphatic alcohols are widely used in various branches of science and technology, quantification of thermodynamic parameters of hydrogen bonding of them with various solutes induces a great practical interest.

Different experimental techniques, such as NMR [2] and infrared [3–5] spectroscopy, vapor pressure measurements [6,7] and solution calorimetry [8–13] were applied for investigation of the hydrogen bonding of various molecules with aliphatic alcohols. However, studies of hydrogen bonding of solute molecules with alcohol clusters in alcohol medium were rather poorly distributed. This task is greatly hampered by some peculiarities of self-associated solvents.

First, the net of hydrogen bonds in associated solvents may be broken while dissolution of some organic molecules in them. This process was discussed in works [3,11–14] and was called reorganization [15]. It was shown that reorganization depends on the solute and solvent molecules structure [12,16,17]. Comparing the number of lone electron pairs capable to hydrogen bonding with a number of active hydrogen atoms in solvent molecule, one may predict the presence (or absence) of reorganization process in it [12]. The type of hydrogen bonding centers (active hydrogen atoms or lone electron pairs) presented in excess determines the type of solute causing the reorganization. Alcohol molecule has two lone electron pairs and one active hydrogen atom. Almost all alcohol molecules are hydrogen bonded with its complexation degree close to 100% [18]. Regardless of association type (open, linear, branched or cyclic) there is a lack of free hydrogen atoms of O–H groups. Consequently, alcohol molecule cannot interact with solute as a proton donor without disruption of alcohol–alcohol hydrogen bonds. However, alcohol molecule possesses a lone electron pair for interacting as a proton acceptor.

Another feature of associated liquids is cooperativity phenomenon [19–22]. Solutes capable to specific interaction form hydrogen bonds with alcohol associates. The energy of such interaction is higher than in equimolar complexes due to cooperative effects [5,7,21,22]. Studies on the hydrogen bonding of amines with alcohols solutions have shown that the cooperative strengthening in complexes of pyridine and its methyl derivatives with alcohols

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